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A perturbation treatment of Percus-Yevick equation and structures of liquid indium and thallium

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A closed form expression for structure factor has been derived, taking the square well potential as a perturbation over the hard-sphere potential. This expression has been used to calculate the structure factor for liquid Indium and Thallium. The agreement between this theory and experiments clearly shows that the concept of pairwise interactions is an useful tool in understanding some of the structural problems of liquid metals and that the representation of the attractive fail by a square well potential is a satisfactory one.

1. Introduction

Recent advances in the theory of transport properties of liquid metals have shown that the structure factor, $S(k)$ plays an important role in their computations (Helfand, 1964; Rao, and Murthy 1975). Recently Egelstaff (1971) have shown that much information regarding the triplet and quadruplet correlation functions can be obtained from the structure factor

2. Theory

The square-well potential can be written as

$$\begin{aligned} U_{sw} &= \infty, && r < \sigma \\ &= -\epsilon, && \sigma < r < \lambda\sigma \\ &= 0, && r > \lambda\sigma \end{aligned} \qquad \ldots (1)$$

where σ is the so-called rigid sphere diameter and ϵ and λ are respectively the depth and breadth of the square well.

We write the square well attractive tail as a perturbation over the hard-sphere. Thus,

$$U_{sw}(r) = U_{hs}(r) + U_1(r) \qquad \ldots (2)$$

where,

$$\begin{aligned} U_{hs}(r) &= \infty, && r < \sigma \\ &= 0, && r > \sigma \end{aligned} \qquad \ldots (3)$$

and

$$\begin{aligned} U_1(r) &= 0, \quad r < \sigma \\ &= -\epsilon, \quad \sigma < r < \lambda\sigma \\ &= 0, \quad r > \lambda\sigma \end{aligned} \qquad \ldots (4)$$

We use the Wertheim-Thiele (1963) hard-sphere potential solution of the direct correlation function (D.C.F.), $C(r)$ for P.Y. equation in the range $0 < r < \sigma$. In this connection we may add that Barker & Henderson (1971) have pointed out that physically the attractive forces in a square well potential can be thought of as providing a back-ground potential in which the molecules move as hard-spheres. Along with others (March 1968, Lebowitz & Percus 1966) we assume that $C(r)$ can be written as

$$C(r) = -U_1(r)/k_BT \qquad \ldots (5)$$

in the range $\sigma < r < \lambda\sigma$

where k_B is the Boltzmann constant and T is the absolute temperature.

We, therefore, write down the D.C.F. of a square well (S.W.) fluid as

$$C_T(r) = C_{hs}(r) + C_{sw}(r) \qquad \ldots (6)$$

The Fourier transform of the Wertheim-Thiele can be written as (Rao & Nammalvar 1975)

$$\begin{aligned} P\tilde{C}_{hs}(K) = &\left[-\frac{.24\eta(1+2\eta)^2}{(1-\eta)^4}\right] \times \left[\frac{\sin k\sigma - k\sigma\cos k\sigma}{(k\sigma)^3}\right] \\ &+\left[\frac{144\eta^2(1+\eta/2)^2}{(1-\eta)^4}\right] \times \left[\begin{array}{l}(-k^2\sigma^2\cos k\sigma + 2k\sigma\sin k\sigma + \\ 2\cos k\sigma - 2)/(K\sigma)^4\end{array}\right] \\ &+\left[\frac{-12\eta^2(1+2\eta)^2}{(1-\eta)^4}\right] \times \left\{\begin{array}{l}(-K^4\sigma^4\cos K\sigma + 4k^3\sigma^3\sin k\sigma + \\ 12k^2\sigma^2\times\cos k\sigma - 24k\sigma\sin k\sigma \\ -24\cos k\sigma + 24)/(k\sigma)^6\end{array}\right\} \end{aligned} \qquad \ldots (7)$$

and that of the square well is

$$P\tilde{C}_{sw}(K) = \left[\frac{24\eta\epsilon}{K_BT}\right] \times [(\sin\lambda k\sigma - \lambda k\sigma\cos\lambda k\sigma + k\sigma\cos k\sigma - \sin k\sigma)/(k\sigma)^3] \qquad \ldots (8)$$

Here $\eta = \pi\rho\sigma^3/6$, where $\rho(= N/V)$ is the no. density. Hence the Fourier transform of the total correlation function is

$$P\tilde{C}_T(K) = P\tilde{C}_{hs}(K) + P\tilde{C}_{sw}(K) \qquad \ldots (9)$$

The structure factor $S(k)$ can be calculated from the relation

$$S(k) = [1 - P\tilde{C}_{\mathcal{T}}(k)]^{-1} \qquad \ldots (10)$$

The potential parameters λ, ϵ and σ can be obtained either by using the compressibility sum rule or by fitting with the experimental data at the first peak position (Rao & Murthy 1975). we have adopted the latter procedure.

3. Results and Discussions

Potential parameters along with temperatures and densities at which calculations have been performed are shown in table 1.

Table 1. Potential parameters

Liquid	Temperature (°K)	Density (atom Å^{-3})	σ (Å)	ϵ/k_B (°K)	λ (Å)
Indium	433	0.03686	2.83	173.76	1.700
Thallium	588	0.03320	2.97	157.97	1.693

The structure factor of liquid Indium at 160°C and liquid Thallium at 315°C are shown in figures 1 and 2 respectively. The agreement obtained between the

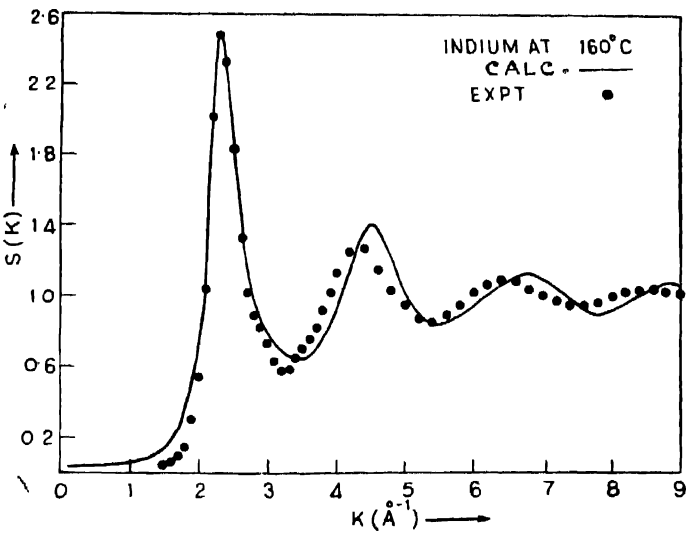

Fig. 1

theory and experiment (Waseda & Suzuki 1973) especially upto the first peak region, which incidentally determines the electronic transport properties of liquid metals (Greenfield & Wiser 1971) is quite encouraging and suggests that the

concept of pairwise interaction is a useful one even in the theory of liquid metals. Except at the second peak where the error is about 12% the agreement in the case of thallium is very good throughout. In the case of Indium there is a slight

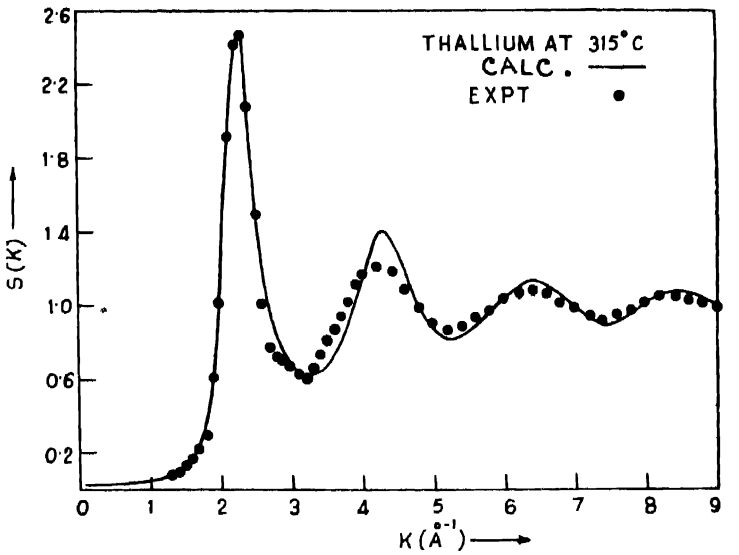

Fig. 2

shift to the right of the second peak position Here also the agreement is within 10%. There is perfect agreement in position and height of the first peak in each case.

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